

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements in and relating to Modified Rubber Compositions

We, THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, a British Body Corporate of 19, Fenchurch Street, London, E.C.3, do hereby declare this invention, for which we

5 pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to modified rubber compositions and the manufacture thereof with more especial reference to polymer modified rubbers.

15 It is well known that some substances notably some types of carbon black and siliceous materials, when incorporated in natural or synthetic rubber confer substantial reinforcement on the vulcanizates. By "reinforcement" is meant the ability of a substance to increase the stiffness and the energy to rupture

20 of a vulcanised rubber composition.

25 More recently it has been discovered that certain synthetic high polymeric substances such as polystyrene and polymethyl methacrylate can similarly reinforce natural rubber. By carrying out the polymerization of one or more monomeric substances in the presence of rubber and catalysts as herein described, rather than by the simple admixture of pre-formed polymer with rubber, an advantage is

30 obtained in that some of the long chain molecules of the polymeric substances become attached to the rubber molecule to give what may be termed a "graft" polymer, which can be visualized as a tree in which the main

35 trunk is the rubber molecule and the branches are molecules of a synthetic polymer.

It had previously been supposed that the mechanism by which the polymer molecules become grafted on to the rubber molecule would proceed in accordance with the well-known transfer reaction whereby the growing

40 polymer chain is terminated by abstraction of

hydrogen from a rubber molecule so producing a rubber radical which can serve as the point of initiation for another polymeric chain. Evidence for this first mechanism has

45 not been obtained since catalysts which serve solely to initiate polymer chains do not produce graft polymers.

The second mechanism, upon which the invention is predicated and which appears to be operative when the catalyst is capable of interaction with rubber, involves growth of a polymer either at the double bond of the rubber molecule, following activation of such

50 double bond by addition of a catalyst radical thereto, or on to a rubber radical produced by abstraction of hydrogen from the rubber molecule by a catalyst radical.

Broadly stated therefore, the present invention consists in the preparation of "grafted" polymers prepared by the polymerization of one or more monomers whose polymerisation is not unduly retarded by rubber, in the presence of rubber and a catalyst which operates

55 according to the second mechanism described above wherein the catalyst is an organic peroxide or hydroperoxide of the types  $R-O-O-R'$  or  $R-O-O-H$  where R and  $R'$  are alkyl, aryl or aralkyl groups used alone or with an activator. The activators, where used, may for instance be reducing agents capable of forming a "redox" system with the peroxide and can advantageously be polyethylene polyamines.

Evidence that the formation of graft polymers results from the second of the two possible mechanisms described above is obtained from an examination of the polymer produced when a catalyst of the class specified under

60 the invention is used compared with a catalyst which does not attack rubber e.g. azoisobutyronitrile (A.Z.B.N.).

Thus, if a 1% solution in benzene of (a) a

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polymer-modified rubber prepared using A.Z.B.N. and (b) the same prepared using a peroxidic catalyst in accordance with the present invention is titrated with methanol containing a trace of calcium chloride then the product of (a) is clearly separable into free rubber and free polymer whereas the graft polymer obtained by (b) shows a novel behaviour whereby, between limits characteristic of each monomer used, a colloidal solution is formed which flocculates at a point short of that where the free polymer precipitates. This former material has been shown (Trans. Far. Soc. 50 (1954) p. 759) to consist solely of rubber molecules with attached polymeric side chains. For proportions of reacted monomer similar to those given in the examples, no free rubber can be separated, all the rubber originally present having been modified by combination with polymer.

Modified rubbers prepared by the process of the invention have valuable properties in that they combine the characteristics of both rubber and plastics and a wide range of materials with properties ranging from those of polymer modified rubbers to rubber modified polymers can be produced.

Especially valuable is the chemical attachment of polymer to rubber obtained in the present invention in that such graft polymers give self-reinforced vulcanizates with outstandingly useful properties such as low hysteresis and excellent resistance to flex cracking and fatigue such as are not obtained in simple physical admixture of polymer with rubber. Similar unique properties are also obtained in foams or cast films prepared directly from the graft polymer latex.

Preferably, the rubber employed is in the form of latex which may be a natural or artificial dispersion of natural rubber or a dispersion of synthetic rubber of rubber-like material.

Preferred monomers are vinyl compounds such as styrene, esters of acrylic and methacrylic acids, acrylonitrile and vinylidene chloride, whose polymerization is not unduly retarded by rubber. Vinyl acetate whose polymerization is heavily retarded by rubber is unsuitable. The monomer, to which the peroxidic catalyst has been added, is stirred into the latex until it has been absorbed into the rubber particles, and polymerisation of the monomer is then effected by the application of heat or the addition of an activating substance, or both. It may be necessary to stabilise the latex either before or after adding the monomer and for this purpose the stabiliser may be anionic, non-ionic or cationic according to the pH at which polymerisation is to be carried out.

The catalyst and its activator should be without deleterious effect on the product, and since it is generally preferred to use latex which has been preserved with ammonia it is

advantageous to select a catalyst which is effective at high pH and which is not inhibited by ammonia or ammonium salts. Especially suitable is a redox system comprising a hydroperoxide such as phenyl-cyclohexyl-, cumyl- or tertiary-butyl- activated by a polyethylene polyamine such as triethylenetetramine or tetra-ethylene pentamine since these systems act efficiently in the presence of ammonia and have the additional advantage of being relatively insensitive to atmospheric oxygen.

Polymerisation may be carried to completion or short-stopped at any convenient stage by adding a short-stopping agent such as chlorodinitrobenzene.

After the reaction has been carried to the desired stage the latex may be compounded with vulcanising ingredients and used as such to deposit self-reinforced rubber articles or to make latex foam of increased stiffness. Alternatively the latex may be coagulated, washed, dried and compounded and cured by orthodox methods to give light-coloured reinforced rubber articles. The degree of reinforcement obtained is dependent on the nature and amount of the monomer used, the greatest reinforcement being obtained with monomers which normally polymerize on their own to give hard polymers.

The properties of the products may be further modified by the use of two different monomers. Especially useful is the introduction of a second monomer containing two polymerisable groups such as divinyl benzene or ethylene dimethacrylate which have the effect of increasing the tear resistance of methacrylate or styrene graft polymers which are otherwise rather poor in this respect especially at more elevated temperatures.

#### EXAMPLE 1.

To 1000 ml. of an ammoniated natural rubber latex containing 30% rubber



and ammonia-content 0.4% was added with stirring a mixture of 119 ml. of methyl methacrylate and 1.3 ml. tert-butyl hydroperoxide. Stirring was continued until a uniform dispersion was obtained (about  $\frac{1}{4}$  hour) and 13.3 ml. of a 10% solution of tetra-ethylene pentamine was stirred in. Stirring was then stopped and the reaction vessel was covered and allowed to stand for 3 hours, during which period there was a small rise of temperature of about 5–10° C. due to the exothermic polymerisation of the monomer. Provided that the vessel was reasonably full no other precautions to exclude air were found necessary.

The polymerised material, which was still a fluid latex, was coagulated by pouring into at least 3 litres of boiling water containing 0.1% of calcium chloride and 1% of acetic acid, and the resulting coarse crumb was hydro-extracted, washed and partially dried

after which it could be sheeted on a mill and further dried by hanging in a warm atmosphere. The yield was 402 g. (98% theory).

- 5 Analysis of the product by the fractional precipitation described above showed that no free rubber was present and half of the polymethylmethacrylate was bound to the rubber in relatively short chains each of molecular weight around 2000 to 5000.

- 10 The dried polymer was compounded on a rubber mill according to the following recipe, which follows standard rubber-compounding practice, and cured for 30 minutes at 140° C.

	Parts
15 Polymer - - - - -	100
Zinc oxide - - - - -	5
Stearic acid - - - - -	1
Sulphur - - - - -	2.5
N-cyclohexyl-2 benzothiazole	
20 sulphenamide - - - - -	0.6
Phenyl-B-naphthylamine - - - - -	1.0

The vulcanized product was a light-coloured reinforced rubber with the following properties:—

- 25 T.S. (tensile strength) - 240 Kg/cm<sup>2</sup>  
 E.b. (elongation at break) - 550%  
 M100 (modulus, 100% extension) - 35 Kg/cm<sup>2</sup>  
 M300 (modulus, 300% extension) - 118 Kg/cm<sup>2</sup>  
 30 Shore hardness - 75  
 Tear resistance, 20° C. - 0.8 Kg/mm  
 Tear resistance, 120° C. - 0.2 Kg/mm  
 Comparative average figures for carbon black reinforced tyre tread compound using the same testing equipment are as follows:—

- 35 T.S. - 272 Kg/cm<sup>2</sup>  
 E.b. - 498%  
 M100 - 32 Kg/cm<sup>2</sup>  
 40 M300 - 153 Kg/cm<sup>2</sup>  
 Shore hardness - 68  
 Tear resistance, 20° C. - 3.0 Kg/mm  
 Tear resistance, 120° C. within range 1.0 to 1.6 Kg/mm  
 45 Into 130 parts of the polymeric product of the above Example 1 was milled 5 parts of di-*t*-butyl peroxide and the mixture was cured for 60 mins. at 153° C. This treatment gave a transparent reinforced rubber with the following properties:—

- 50 Tensile strength - 126 Kg/cm<sup>2</sup>  
 M100 - 42 Kg/cm<sup>2</sup>  
 E.b. - 298%  
 Hardness B.S.I. - 79  
 55 **EXAMPLE 2.**  
 A graft-polymer latex prepared substantially as in Example 1 but at a final solids content of 60% was mixed with ordinary 60% natural rubber latex concentrate to give a final  
 60 methylmethacrylate concentration of 9%. To an amount of this mixture containing 109 parts by weight of solids was added in this order 0.5 parts sodium ricinoleate (in 20% solution) for stabilisation, and a 50% aqueous

dispersion of a mixture of 2 parts sulphur 0.5 parts zinc salt of mercaptobenzthiazole with 0.2 parts of zinc diethyl dithiocarbamate. This mixture was foamed to six times its original volume and to it was added successively 50% aqueous dispersions of 1.8 parts zinc oxide and 0.5 parts sodium silicofluoride. Stirring was then slowed down to refine the foam during 1 minute after which the foam was poured into a mould, allowed to gel for 10 minutes and cured at 100° C. for 60 minutes. The resulting foam had a compression modulus of 0.2 kilograms/sq. cm. at 60% compression whereas ordinary latex foam of the same density has a compression modulus of only 0.1 kilogram/sq.cm. at 60% compression.

### EXAMPLE 3.

To 750 ml. of an ammoniated natural rubber latex concentrate of 60%  $\left(\frac{W}{W}\right)$  rubber content and 0.8% ammonia content was added 750 ml. of water and 150 ml. of a 10% aqueous solution of ammonium caseinate. Styrene (150 g.) to which had been added *t*-butyl hydroperoxide (1.1 g.) was stirred into the latex for  $\frac{1}{2}$  hour after which 11 g. of a 10% aqueous solution of tetra-ethylene pentamine was stirred in. Stirring was stopped, the reaction vessel was covered as in Example 1 and polymerisation was allowed to proceed at 60° C. After 5 hours the polymerisation was substantially complete and the product was coagulated, washed and dried as in Example 1.

Analysis of the product as in Example 1 showed no free rubber and a substantial part of the styrene bound to rubber, again in relatively short chains.

When compounded as in Example 1 the styrene graft polymer gave the following data:—

T.S. - - - - -	249 Kg/cm <sup>2</sup>
E.b. - - - - -	618%
M100 - - - - -	25 Kg/cm <sup>2</sup>
M300 - - - - -	61 Kg/cm <sup>2</sup>
Hardness - - - - -	70

Latex foam prepared from the ethylene graft polymer latex after dilution to 5 to 10% styrene content gave foams of increased rigidity similar to that described in Example 2.

### EXAMPLE 4.

Methyl methacrylate containing 1 g. of benzoyl peroxide per litre was added in various proportions to ammoniated natural rubber latex containing 30% rubber stabilised by the prior addition of 1.7 parts of the material sold under the Registered Trade Mark of Lubrol W per 100 parts rubber in the latex. The mixtures were heated to 80–90° C. for 4 hours after which unreacted monomer was removed by steam distillation. Products very similar to those of Example 1

were obtained by the method, but only 60—70% of the methyl methacrylate was polymerised under the conditions of the present example.

#### EXAMPLE 5.

To 400 grams of an ammoniated natural rubber latex containing 30% rubber (w/w) and ammonia content 0.4% was added gradually with stirring a mixture of 120 grams uninhibited ethyl acrylate and 0.44 ml. of *tert*-butyl hydroperoxide of 70% purity. Stirring was continued until a uniform dispersion was obtained (about  $\frac{1}{4}$  hour). This operation was performed in an open glass vessel. At this stage the vessel was closed with a bung and fitted with a glass tube going to the bottom of the vessel and a short glass exit tube, and was immersed in a 30° C. bath. Commercial nitrogen was then passed through the longer tube, thus freeing the vessel of oxygen and also serving to stir the contents of the vessel. After 5 minutes 4.0 ml. of a fresh 10% aqueous solution (w/w) of tetra-ethylene pentamine was added and reaction started within a few minutes, the temperature rising ultimately to about 35° C. and then dropping back to 30° C. After the first 10 minutes the nitrogen flow was reduced to a few bubbles per second.

In this example the reaction was allowed to go to completion by leaving for 20 hours at 30° C. corresponding to a conversion of 65%. The semi-solid reaction mixture was then cut up and added to 2½ litres of hot water containing 2½ grams calcium chloride. The product was filtered off, partially air dried, sheeted on the mill and air-dried again for several days.

When this dry product is passed through a rubber mill with 0.005—0.010" nip it behaves in a peculiar manner, flowing out to give a thin sheet with very little tensile strength or stiffness compared with ordinary rubber. This effect is referred to as "sheeting". When this material is compounded with the usual vulcanizing ingredients and heated at 140° C. it has such poor tensile strength that the test piece breaks before an extension of 100% can be reached. The unvulcanised product has however very good ageing properties when exposed in a K.B.B. fugitometer or when exposed at 50° C. to the light of a cold mercury arc.

When this material is modified by "short-stopping" as given in the next example, the good ageing can be retained while the "sheeting effect" disappears and the product can then be vulcanized.

#### EXAMPLE 6.

The procedure of Example 4 is followed precisely, except that after the tetra-ethylene pentamine has been added the reaction is allowed to proceed for 180 minutes only, when 0.6 gram of chlorodinitrophenol (or other suitable substance) in 10 ml. ethyl acrylate mono-

mer is added to "short-stop" the reaction. The nitrogen stream is increased to agitate and mix the contents of the vessel which are still dispersed as a latex. The contents are then poured into 2½ litres of hot water + 2½ grams calcium chloride. The coagulum is then separated and cut up, partially dried, sheeted and dried in air as before. The degree of conversion of the monomer initially added is 45—50%. This product when passed through the tight nip of a rubber mill behaves similarly to ordinary rubber and does not "sheet".

When vulcanized it gives roughly the same modulus (M100 of 8—11) as ordinary gum stock but in addition has very good ageing properties to light and heat.

#### EXAMPLE 7.

To 1000 ml. of an ammoniated natural rubber latex containing 30% rubber  $\left( \begin{smallmatrix} W \\ - \\ W \end{smallmatrix} \right)$

and ammonia-content 0.4% was added with stirring a mixture of 106 ml. of methylmethacrylate, 13 ml. of washed and redistilled commercial divinylbenzene (containing 40% divinylbenzene) and 1.3 ml. *tert*-butyl hydroperoxide. Stirring was continued until a uniform dispersion was obtained (about  $\frac{1}{4}$  hour) and 13.3 ml. of a 10% solution of tetra-ethylene pentamine was stirred in. Stirring was then stopped and the reaction vessel was covered and polymerisation was allowed to proceed as in Example 1. The product was isolated and dried as in previous examples. When compounded and cured according to the procedure given in Example 1 a vulcanizate of improved tear resistance was obtained as exemplified by the following data:—

T.S.	- - - - -	257 Kg/cm <sup>2</sup>	
E.b.	- - - - -	530%	
M100	- - - - -	37 Kg/cm <sup>2</sup>	
M300	- - - - -	107 Kg/cm <sup>2</sup>	105
Hardness	- - - - -	78	
Tear resistance, 20° C.	-	3.4 Kg/mm	
Tear resistance, 120° C.	-	0.7 to 1.75 Kg/mm	

#### EXAMPLE 8.

To 100 g. of a synthetic butadiene-styrene copolymer latex (GRS latex type IV) containing 43 g. copolymer was added 12.5 g. of methyl methacrylate containing 0.08 g. *t*-butyl hydroperoxide and, when homogeneous, 0.08 g. of tetra-ethylene pentamine in aqueous solution was added. After 3½ hours 72% of the monomer had polymerised and the product, isolated as in Example 1, gave the following data:—

T.S.	- - - - -	121 Kg/cm <sup>2</sup>	120
E.b.	- - - - -	378%	
M100	- - - - -	14 Kg/cm <sup>2</sup>	
M300	- - - - -	75 Kg/cm <sup>2</sup>	

whereas the synthetic rubber isolated from the untreated latex gave the following data:—

T.S. - - - - - 35 Kg/cm<sup>2</sup>  
 E.b. - - - - - 498 %  
 M100 - - - - - 8 Kg/cm<sup>2</sup>  
 M300 - - - - - 19 Kg/cm<sup>2</sup>

5 What we claim is:—

1. A process for the preparation of modified rubbers by the polymerisation of one or more monomers, whose polymerisation is not unduly retarded by rubber, in the presence of  
 10 rubber and a catalyst which promotes growth of a polymer, either at the double bond of the rubber molecule, following activation of such double bond by addition of a catalyst radical thereto, or on to a rubber radical produced by  
 15 abstraction of hydrogen from the rubber molecule by a catalyst radical wherein the catalyst employed is an organic peroxide or hydroperoxide of the types R—O—O—R<sup>1</sup> or  
 20 R—O—O—H where R and R<sup>1</sup> are alkyl, aryl or aralkyl groups.

2. A process according to the preceding claim employing as activator a reducing agent e.g. polyethylene polyamine capable of forming a "redox" system with the peroxide.

3. A process for the preparation of modified rubbers according to Claim 1 wherein the rubber is reinforced by graft polymerisation as herein defined of a monomer which normally  
 25 polymerises to give a hard polymer, in the presence of a peroxide catalyst.

4. Cast or foamed products obtained from latex by the process according to Claim 3.

5. A process according to any of Claims 1 to 4 wherein the polymerisation is carried to  
 30 completion.

6. A process according to any of Claims 1 to 4 wherein the polymerisation is short-stopped by adding an agent such as chloro dinitrobenzene.

7. Processes for the preparation of modified rubber substantially as described in any of  
 40 Examples 1 to 8 herein.

8. Modified rubbers when prepared according to any of Examples 1 to 8 herein.

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## PROVISIONAL SPECIFICATION

### Improvements in and relating to Modified Rubber Compositions

45 We, THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, a British Body Corporate of 19, Fenchurch Street, London, E.C.3, do hereby declare this invention, to be described in the following statement:—

50 This invention relates to modified rubber compositions and the manufacture thereof with more especial reference to polymer modified rubbers having enhanced tear resistance.

55 It is well known that some substances, notably some types of carbon black and siliceous materials, when incorporated in natural or synthetic rubber confer substantial reinforcement in the vulcanizates. By "reinforcement" is meant the ability of a substance to increase  
 60 the stiffness and the energy to rupture of a vulcanised rubber composition.

65 More recently it has been discovered that certain synthetic high polymeric substances such as polystyrene and polymethyl-methacrylate can similarly reinforce natural rubber. By carrying out the polymerisation of the monomeric substances in the presence of rubber, rather than by the simple admixture  
 70 of pre-polymerised polymer with rubber, an advantage is obtained in that some of the long chain molecules of the polymeric substances become attached to the rubber molecule to give what is now known as a "graft" polymer, which can be visualized as a tree in which  
 75 the main trunk is the rubber molecule and the branches are molecules of a synthetic polymer.

80 The mechanism of the reaction by which the polymer molecules become "grafted" on to the rubber molecule can proceed in either or both of two ways, according to the catalyst

85 system and polymerisation conditions used. In the presence of catalysts which have no action on the rubber, the decomposition of the catalyst initiates polymerisation of the monomeric substances and polymerisation follows a normal course until the growing radical head of the polymer is terminated by abstraction of hydrogen from a rubber molecule, so producing a rubber radical which can serve as the locus of growth of another polymeric chain. This is, essentially, the well known transfer reaction  
 90 between a growing polymer and a hydrogen donor, and it results in the formation of free polymer as well as polymer attached to rubber (i.e. the desired "graft" polymer).

95 The second mechanism, which appears to be operative when the catalyst is capable of interaction with rubber, involves growth of a polymer either at the double bond of the rubber molecule, following activation of such double bond by addition of a catalyst radical thereto, or onto a rubber radical produced by abstraction of hydrogen from the rubber molecule by a catalyst radical. Evidence for the second course of reaction is obtained from a study of the composition of the "graft" polymer, which reveals that considerably more polymer is combined with the rubber than can be explained by a simple transfer reaction. Formation of free polymer by direct attack of catalyst on monomer again accompanies the formation of the "graft" polymer.

100 105 110 115 Compositions prepared by any of the foregoing methods have valuable properties in that they combine the characteristics of both rubber and plastics and a wide range of

materials with properties ranging from those of polymer modified rubbers to rubber modified polymers can be produced. Especially valuable is the production of a "graft" polymer in which the synthetic polymeric material is chemically combined with the rubber, in that rubbery graft polymers exhibit, after vulcanization, low hysteresis.

- 5  
10  
15  
20
- Vulcanizates of rubbery polymeric compositions made by any of the foregoing methods are deficient in one important property, namely, tear resistance and more particularly, tear resistance at elevated temperatures. The present invention overcomes this important defect by the addition of a second monomer, containing two polymerisable groups, such as divinylbenzene or ethylenedimethacrylate and subsequently co-polymerising the two monomers in the presence of rubber, which may be masticated rubber, dissolved rubber or rubber latex.

- 25  
30  
35
- The purpose of the second monomer is to cross-link the long chain molecules of the synthetic polymer and from the foregoing account of the formation of "graft" polymers, it will be obvious that such cross-linking will effectively bind the free polymer into the "graft" polymer system. That this actually occurs is easily proved by subjecting the "graft" polymer to solvent extraction, when it can be demonstrated that no free polymer can be separated and the polymer-modified rubber is indeed substantially insoluble, whereas similar compositions made in the absence of the second monomer are soluble.

- 40
- Broadly stated, therefore, the process of making polymer modified rubbers according to the invention consists essentially in the step of including a monomer containing two polymerisable groups in the rubber-monomer composition which is to be polymerized.

- 45
- Preferably, the rubber employed is in the form of latex which may be a natural or artificial dispersion of natural rubber or a dispersion of synthetic rubber or rubber like material, and preferably also the polymerisation is effected with the aid of a peroxide catalyst and with the monomer dispersed in the latex.

- 50
- On coagulation, drying, and subsequent vulcanization modified rubbers are obtained having enhanced properties, particularly as regards tear resistance as shown by the following example:—

#### EXAMPLE

- 55  
60
- To 1000 ml. of an ammoniated natural rubber latex containing 30% rubber  $\left( \begin{smallmatrix} W \\ - \\ W \end{smallmatrix} \right)$  and ammonia-content 0.4% was added with stirring a mixture of 106 ml. of uninhibited methylmethacrylate, 13 ml. of a washed and redistilled commercial divinylbenzene concentrate containing 40% divinyl benzene and 1.3 ml. tert-butyl hydroperoxide. Stirring

was continued until a uniform dispersion was obtained (about  $\frac{1}{2}$  hour) and 13.3 ml. of a 10% solution of tetra-ethylene pentamine was stirred in. Stirring was then stopped and the reaction vessel was covered and allowed to stand for 3 hours, during which period there was a small rise of temperature of about 5–10° C. due to the exothermic polymerization of the monomers. Provided that the vessel was reasonably full no other precautions to exclude air were found necessary.

The polymerized material, which was still a fluid latex, was coagulated by pouring into at least 3 litres of boiling water containing 1% of calcium chloride and 1% of acetic acid, and the resulting coarse crumb was hydro-extracted, washed and partially dried after which it could be sheeted on a mill and further dried by hanging in a warm atmosphere. The yield was 402 g. (99.5% theory).

The dried polymer was compounded on a rubber mill according to the following recipe, which follows standard rubber-compounding practice and cured for 30 minutes at 140° C.

	Parts	
Polymer - - - - -	100	
Zinc oxide - - - - -	5	90
Stearic acid - - - - -	1	
Sulphur - - - - -	2.5	
N-cyclohexyl-2 benzothiazole		
sulphenamide - - - - -	0.6	
Phenyl-naphthylamine - - - - -	1.0	95
Test samples from this compound had the following properties:—		
Tensile strength - - - - -	257 Kg/cm <sup>2</sup>	
Elongation at break - - - - -	530%	
Modulus, 100% extension - - - - -	37 Kg/cm <sup>2</sup>	100
Modulus, 300% extension - - - - -	107 Kg/cm <sup>2</sup>	
Shore hardness - - - - -	78	
Tear resistance, 20° C. - - - - -	3.4 Kg/mm	
Tear resistance, 120° C. within range 0.7 to 1.75 Kg/mm		105

For comparison, a similar vulcanized polymer in which the divinylbenzene had been omitted and an extra 13 ml. of methylmethacrylate used in its place had the following properties:—

Tensile strength - - - - -	240 Kg/cm <sup>2</sup>	110
Elongation at break - - - - -	550%	
Modulus, 100% extension - - - - -	35 Kg/cm <sup>2</sup>	
Modulus, 300% extension - - - - -	118 Kg/cm <sup>2</sup>	
Shore hardness - - - - -	75	115
Tear resistance, 20° C. - - - - -	0.8 Kg/mm	
Tear resistance, 120° C. - - - - -	0.2 Kg/mm	

The poor tear-resistance here obtained clearly demonstrates the advantageous effect of the divinylbenzene in the previous composition.

Comparative average figures for carbon black reinforced tyre tread compound using the same testing equipment are as follows:—

Tensile strength - - - - -	272 Kg/cm <sup>2</sup>	125
Elongation at break - - - - -	498%	
Modulus, 100% extension - - - - -	32 Kg/cm <sup>2</sup>	
Modulus, 300% extension - - - - -	153 Kg/cm <sup>2</sup>	

Shore hardness - - - 68  
Tear resistance, 20° C. - 3.0 Kg/mm  
Tear resistance, 120° C. within range 1.0  
to 1.6 Kg/mm

herein defined, and that the vulcanizates  
obtained according to the invention have a 10  
variety of uses.

- 5 It will be understood that the invention is  
not limited to the particular example, that the  
ingredients and proportions may be varied  
without departing from the invention as

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